PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 35,252	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 03/38469	International filing date *(day/month/year)* 01.12.2003	Priority date *(day/month/year)* 01.12.2003
International Patent Classification (IPC) or both national classification and IPC C22C1/04		
Applicant EXTRUDE HONE CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the opinion
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   VI ☐ Certain documents cited
   VII ☐ Certain defects in the international application
   VIII ☐ Certain observations on the international application

Date of submission of the demand 16.12.2004	Date of completion of this report 26.01.2006
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Alvazzi Delfrate, M Telephone No. +49 89 2399-8444

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-14	as originally filed
15-20	filed with telefax on 14.11.2005

Claims, Numbers

1-29	filed with telefax on 14.11.2005

Drawings, Sheets

1/3-3/3	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

   see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	21
Inventive step (IS)	Yes:	Claims	
	No:	Claims	22-29
Industrial applicability (IA)	Yes:	Claims	1-29
	No:	Claims	

2. Citations and explanations

   see separate sheet

Reference is made to the following document/s/:

D1: SCHAFFER G B ET AL: "THE INFLUENCE OF THE ATMOSPHERE ON THE SINTERING OF ALUMINUM" METALLURGICAL AND MATERIALS TRANSACTIONS A: PHYSICAL METALLURGY &MATERIALS SCIENCE, THE MINERALS, METALS AND MATERIALS SOCIETY, US, vol. 33A, no. 10, October 2002 (2002-10), pages 3279-3284, XP009037316 ISSN: 1073-5623

D2: AMATO I ET AL: "SINTERING PROCEDURES FOR ALUMINIUM P/M PARTS AND METALLOGRAPHIC EXAMINATION DURING THE PROCESS" POWDER METALLURGY, METALS SOCIETY. LONDON, GB, vol. 19, no. 3, 1976, pages 171-176, XP009037274 ISSN: 0032-5899

D3: Wronski et al. "The determination of fracture strength from ultimate tensile and transverse rupture stresses" in Powder Metallurgy Progress, Vol. 3 (2003), n. 3, abstract

D4: Ma et al. "Mechanical Properties of Fine-Grained P/M Aluminum"in Proceedings of the 6th Asia Pacific Symposium on Engin. Plasticity and its Applications (AEPA 2002), Key Engineering Materials 2003

1. No basis could be found in the application documents as filed for the feature inserted by amendment in claim 21 that no evidence of consolidating the powder by hot isostatic pressing is present. No basis has been found either for the corresponding newly introduced paragraph 44 bis of the description. According said amendments are not considered for establishing this report (Art. 34(2) (b) PCT and R. 70.2(c) PCT).

2. Claim 21 is unclear because no precise value and no measuring technique are given to indicate which compositional gradients and which particle deformation are acceptable. As far as the particle deformation is concerned paragraph 44 refers to the alumina film boundaries. It is however to be noted that said boundaries will usually differ from the boundaries of the grains of the densified body; moreover no indication is given for all the cases where such boundaries are not detectable any more. As to which compositional is to be seen as evidence of use of a sintering aid no concrete indication is provided.

3. D1, disclosing the use of nitrogen atmosphere for sintering Al parts is regarded as the

closest prior art for the process claim 1.

The claimed process is rendered novel by the addition of water vapour in the claimed amount.

Such novel feature results in improved sintering (cf. examples of the present application) and is neither disclosed nor suggested by the available prior art.

4. A sintered Al-based article having a tensile strength in the range claimed in claim 21 is known in the art, for instance from D2 (table II, Figures 5-6), which does not mention concentrations gradients and particle deformation. Accordingly, the subject-matter of claim 21 is not novel. Slight anisotropies that may be present in the microstructures of Fig. 5 and 6 can be seen as statistical variations of a generally isotropic structure and cannot be regarded as "evidence of particle deformation having occurred by an application of a mechanical force prior to or during sintering". Of course the material of D2 does not show evidence that no particle deformation has been applied either (however such an evidence may look like); but since the claim requires merely a lack of evidence it is sufficient, for its claimed subject-matter to lack novelty, that the skilled practitioner is not confronted with information unambiguously pointing out to said mechanical deformation. The table II indicates a value of tensile strength which implies a transverse strength within the claimed range because the transverse strength is higher than the tensile strength (cf. D3).

5. Moreover, the subject-matter of claim 21 is also known from D4, disclosing (Experimental Procedure) the production by HIP of sintered parts from Al powder. The strength values are within the claimed range (Results and Discussion). No sintering additive is used. Since the HIP is isotropic, there is no anisotropy in the sintered compact that can be seen as evidence of the particle deformation due to a mechanical force. Nor it can be seen which other features may be seen as evidence of the application of HIP.

6. The dependent claims 22-29 add features being either known from D2 or standard in the art. Accordingly, they do not relate to novel and inventive subject-matter.

examining the microstructure of the sintered article to determine the shape of the prior particle boundaries as outlined by the alumina that made up the films that enveloped the particles prior their sintering together. The prior particle boundary shapes will correspond to those of the undeformed aluminum powder where no mechanical force has been applied.

[44bis] Persons skilled in the art recognize that hot isostatic pressing of a mass of aluminum powder causes the aluminum powder particles comprising it to suffer deformation under an isostatically applied mechanical force as the mass densifies and sinters together. Accordingly, such persons would recognize that evidence that a aluminum powder has been consolidated by hot isostatic pressing is itself evidence that the aluminum powder particles were deformed by mechanical force prior to or during sintering. Such evidence includes any that a person skilled in the art would recognize, including microstructural artifacts such as grain growth patterns, porosity shape and distribution, and prior particle boundary characteristics.

[45] The aluminum powder comprising such articles may be either pure aluminum or an aluminum alloy. It also may be a mixture of particles of pure aluminum and one or more aluminum alloys or may be a mixture of various aluminum alloys. There are no restrictions on the composition of the aluminum powder other than it is to contain sufficient aluminum in metallic form for the powder particles to form a substantially enveloping film of alumina.

[46] The articles that are embodiments of the present invention may also comprise one or more ceramics in their microstructures. Such ceramics include, without limitation, alumina, silica, silicon carbide, boron nitride, and refractory metal carbides, e.g., tungsten carbide. The amount and size of the ceramic powder is

controlled so as to permit the desired amount of sintering of the aluminum powder to be achieved.

[47] The desired relative density of such an article will depend upon the aluminum powder parameters and the application for which the article is intended to be used. In some cases, for example where the article will be used as a filter, a low relative density, e.g., about 40%, may be desirable. In other applications, higher relative densities are desirable as they provide for greater strength. In general, where article strength is a major consideration, a relative density of at least about 60% is preferred. More preferably, the relative density is at least about 75%, even more preferably it is at least about 85%, and most preferably it is at least about 95%.

Example 1

[48] Two samples of a commercially pure aluminum powder, grade UN No. 1396, were provided. The aluminum powder was spherical and had an average particle size in the range of 17 to 30 microns. Each sample was placed into a cylindrical alumina crucible, approximately 2.54 cm in diameter by 6.35 cm high and tapped lightly to settle the aluminum powder. Each sample was heated in a small box furnace capable of atmosphere control at a rate of 5° C/minute to the sintering temperature, held at the sintering temperature of 630° C for 1 hour and then cooled to room temperature at approximately 5° C/minute. The atmosphere in the furnace was nitrogen containing a preselected partial pressure of water vapor.

[49] One sample was processed in a nitrogen atmosphere in which the preselected water vapor partial pressure was essentially nil. No sintering was observed in this powder. In comparison, a sample that was processed with a preselected water vapor pressure of 0.014 kPa sintered to a relative density of 74.4%.

Example 2

[50] Three samples of commercially pure aluminum powder as in Example 1 were processed as in Example 1, except that the sintering temperature was 635° C. A first sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.004 kPa. This sample sintered to a relative density of 83.3%. A second sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.009 kPa. This sample sintered to a relative density of 80.8%. A third sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.018 kPa. This sample sintered to a relative density of 74.9%.

Example 3

[51] Two samples of commercially pure aluminum powder as in Example 1 were processed as in Example 1, except that the sintering temperature was 640° C. One sample was processed in a nitrogen atmosphere having a preselected water vapor partial pressure of 0.004 kPa. This sample sintered to a relative density of 75.3%. The other sample was processed in a nitrogen atmosphere having a preselected water vapor partial pressure of 0.017 kPa. No sintering was observed in this sample.

Example 4

[52] Two samples of aluminum powder of alloy UN No. 6061 were provided. The composition of the aluminum powder was, in weight percent: aluminum, balance; chromium, 0.07; copper, 0.25; iron, 0.25; magnesium, 0.89; manganese, 0.03; silicon, 0.65; titanium, 0.02; and vanadium, 0.01. The particle size distribution was, in weight percent: +140 mesh (> 106 microns), 0.2; −140 mesh/+170 mesh (< 106 microns/ > 90 microns), 4.8; −170 mesh/+200 mesh (< 90 microns/ > 75

microns), 9.2; −200 mesh/+325 mesh (< 75 microns/ > 45 microns), 77.6; and −325 mesh (< 45 microns), 8.2.

[53] The samples were processed as in Example 1, including the 630° C sintering temperature and the preselected levels of water vapor partial pressures. The sample that was processed in a nitrogen atmosphere in which the preselected water vapor partial pressure was essentially nil showed no sintering of the aluminum powder. The sample that was processed in a nitrogen atmosphere in which the preselected water vapor pressure was 0.014 kPa sintered to a relative density of 64.3%.

Example 5

[54] Two samples of 6061 aluminum powder as in Example 4 were processed as in Example 2, including the sintering temperature of 635° C and the preselected levels of water vapor partial pressures. A first sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.004 kPa. This sample sintered to a relative density of 85.4%. A second sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.009 kPa. This sample sintered to a relative density of 99.1%. A third sample was processed in a nitrogen atmosphere having a preselected water vapor pressure of 0.018 kPa. This sample sintered to a relative density of 78.6%.

[55] FIG. 1 shows a graph of sintered density as a function of the water vapor partial pressure in the nitrogen atmosphere for this experiment. FIG. 2 illustrates the dense microstructure of the sample that was processed in a nitrogen atmosphere having 0.009 kPa partial pressure of water vapor to achieve a relative

density of 99.1%. The etchant used for the microstructure in FIG. 2 was, by volume, 10 parts nitric acid, 1 part hydrofluoric acid, and 89 parts water.

Example 6

[56] Two samples of 6061 aluminum powder as in Example 4 were processed as in Example 3, including the sintering temperature of 640° C and the preselected levels of water vapor partial pressures. One sample was processed in a nitrogen atmosphere having a preselected water vapor partial pressure of 0.004 kPa. This sample sintered to a relative density of 84.2%. The other sample was processed in a nitrogen atmosphere having a preselected water vapor partial pressure of 0.017 kPa. No sintering was observed in this sample.

Example 7

[57] Five samples of 6061 aluminum powder as in Example 4 were processed as in Example 1, except the sintering temperatures were varied between 600° C and 645° C and the partial pressure of water vapor in the nitrogen atmosphere was kept constant at 0.004 kPa. No test was conducted at a sintering temperature of 630° C. The relative densities of the samples after sintering were:

Sintering Temperature	Relative Density
600° C	56.9 %
620° C	66.5%
635° C	85.4%
640° C	84.2%
645° C	86.3%

[58] FIG. 3 shows the relative densities of these samples after sintering as a function of the sintering temperature.

[59] The foregoing examples demonstrate that the present invention may be employed to sinter both pure aluminum powder and alloy aluminum powder. They also show that the present invention is operative over a range of particle sizes and highlight the criticality of the identified range of the partial pressure of the water vapor in the nitrogen sintering atmosphere.

[60] While only a few embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that many changes and modifications may be made thereunto without departing from the spirit and scope of the invention as described in the following claims. All United States patents referenced in this specification are included herein by reference as if they were set forth in full herein .

Claims

What is claimed is:

1. A process for sintering aluminum powder comprising the steps of:

a) providing an aluminum powder; and

b) heating said aluminum powder, in an atmosphere consisting primarily of nitrogen, at a predetermined temperature and a predetermined time to sinter said aluminum powder to a transverse rupture strength of at least about 13.8 MPa, wherein said atmosphere contains a partial pressure of water vapor in the range of about 0.001 kPa to about 0.02 kPa;

wherein said aluminum powder is not pressed together by a mechanical force that substantially deforms the particles of said aluminum powder prior to or during said step of heating.

2. The process of claim 1, wherein said aluminum powder has a composition consisting essentially of aluminum.

3. The process of claim 1, wherein said aluminum powder is an aluminum alloy.

4. The process of claim 1, further comprising the step of mixing said aluminum powder with ceramic powder.

5. The process of claim 4, wherein said ceramic powder includes at least one selected from the group consisting of alumina, silica, silicon carbide, boron nitride, and refractory carbides.

6. The process of claim 1, further comprising the step of mixing said aluminum powder with a sintering aid.

7. The process of claim 6, wherein the composition of said sintering aid includes at least one selected from the group consisting of magnesium and tin.

8. The process of claim 1, further comprising the step of forming said aluminum powder into a shape prior to said step of heating.

9. The process of claim 8, wherein said step of forming includes containerization of said aluminum powder.

10. The process of claim 8, wherein said step of forming includes metal injection molding of said aluminum powder.

11. The process of claim 8, wherein said step of forming includes forming said aluminum powder by a layered manufacturing technique.

12. The process of claim 11, wherein the layered manufacturing technique includes the three-dimensional printing (3DP) process.

13. The process of claim 11, wherein the layered manufacturing technique includes the selective laser sintering (SLS) process.

14. The process of claim 1, wherein said partial pressure of the water vapor is in the range of about 0.003 kPa to about 0.015 kPa.

15. The process of claim 1, wherein said aluminum powder consists of particles in the size range of between about 1 micron to about 500 microns.

16. The process of claim 15, wherein the size range of said aluminum powder particles is between about 45 microns and 106 microns.

17. The process of claim 1, wherein in the step of heating, said aluminum powder is sintered to a relative density of at least about 60%.

18. The process of claim 1, wherein in the step of heating, said aluminum powder is sintered to a relative density of at least about 75%.

19. The process of claim 1, wherein in the step of heating, said aluminum powder is sintered to a relative density of at least about 85%.

20. The process of claim 1, wherein in the step of heating, said aluminum powder is sintered to a relative density of at least about 95%.

21. An article comprising sintered aluminum powder, said sintered aluminum powder having a transverse rupture strength of at least about 13.8 MPa and a microstructure which contains no compositional concentration gradients indicative of the use of a sintering aid and no evidence of particle deformation having occurred by an

application of a mechanical force prior to or during sintering, including no evidence that the aluminum powder was consolidated by hot isostatic pressing.

22. The article of claim 21, wherein said aluminum powder has a composition consisting essentially of aluminum.

23. The article of claim 21, wherein said aluminum powder is an aluminum alloy.

24. The article of claim 21, wherein said article further comprises a ceramic.

25. The article of claim 24, wherein said ceramic includes at least one selected from the group consisting of alumina, silica, silicon carbide, boron nitride, and refractory carbides.

26. The article of claim 21, wherein said article has a relative density of at least about 60%.

27. The article of claim 21, wherein said article has a relative density of at least about 75%.

28. The article of claim 21, wherein said article has a relative density of at least about 85%.

29. The article of claim 21, wherein said article has a relative density of at least about 95%.